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54 Tobacco filter.

57 For the removal of harmful and hazardous substances, particularly suspected carcinogens, contained in tobacco smoke, a tobacco filter is proposed which contains a phthalocyanine compound, with or without a highly water-absorbing material, in the conventional material of a tobacco filter.

EP 0 121 436 A2

TOBACCO FILTER

This invention relates to a tobacco filter which has a high rate of removal for harmful and hazardous substances contained in tobacco smoke.

5 For materials of tobacco filter, various kinds have so far been proposed, such as cellulose acetate, paper, rayon, polypropylene, etc., and some of those materials have already been in practical use, but they are not necessarily the satisfactory materials for tobacco filter, when
10 viewed from the removal effect of harmful or hazardous substances, particularly carcinogenic substances, contained in tobacco smoke.

 Various proposals have been made for the removal
15 of harmful substances in tobacco smoke, such as a method to add hemin compounds containing trivalent iron to the material of filter (Japanese Unexamined Published Patent Application 39767/1982), a method to add L-ascorbic acid stearate (Japanese Unexamined Published Patent Application
20 48700/1973), a method to add cyclodextrin (Japanese Unexamined Published Patent Application 125100/1975), etc.

 As a result of the studies made on a filter which substantially removes harmful and hazardous sub-
25 stances particularly the suspected carcinogens contained in tobacco smoke, the inventors have discovered that the said objective can be achieved by allowing a phthalocyanine compound present in the filter material.

30 The present invention is, therefore, in a tobacco filter which is characterized by that a phthalocyanine compound, or a phthalocyanine compound with a highly water-absorbing material, is present in the material of tobacco filter.

In this invention, in order to have the phthalocyanine compound presented in the filter material, various methods may be available, such as a method to add the phthalocyanine compound per se into the filter material, a method to have the phthalocyanine compound adhered to the filter material, a method to have it chemically bound to the filter material, and a method to insert a member made of other material to which the phthalocyanine compound is adhered or combined, into the filter material.

In this invention, "phthalocyanine" which constitutes the phthalocyanine compound may be such phthalocyanines as non-metallic, and those containing copper, nickel, cobalt, aluminum, iron, etc.

The phthalocyanine compound in this invention is well known in the dyestuff and pigment industries, and in this invention, it is advantageous to use the phthalocyanine compound such as phthalocyanine pigments, phthalocyanine direct dyes, phthalogen dyes, sulfur dyes, vat dyes, reactive dyes, etc.

Dyestuffs other than reactive dyes and pigments are suitable for being added or made to adhere (dyeing) to the material, while reactive dyes are suitable for being chemically bound to the base material.

In this invention, the filter material may be any of known products such as cellulose acetate, cotton, paper, rayon, polypropylene, and water, or other materials such as protein, polyamide, polyvinyl alcohol and its modified products, silica gel, and polystyrene. These materials may be used in the form of fiber, powder, beads, solution, etc.

Especially, the material suitable for binding

reactive dyes may be organic or inorganic substances having hydroxy group, amino group, mercapto group or carboxylamide group, for example, polysaccharides, e.g. cellulose, starch, Sepharose made by Pharmacia Co., etc., proteins, e.g. wool, silk, etc., polyamides, e.g. nylon, polyacrylamide, etc., polyvinyl alcohol or its modified products, silica gel, etc. The phthalocyanine compound is appropriately added, or made to adhere or to chemically bind to these materials by the known methods.

In this invention, it is advantageous to blend a highly water-absorbing material in the form of fiber or powder with the filter material during the course of its making. Such water-absorbing material is used to hold the moisture in the filter during smoking. It may be used in a fairly large amount, but, from the viewpoint of maintaining the strength of the fiber, the amount is preferably not more than 10 wt.% of the filter.

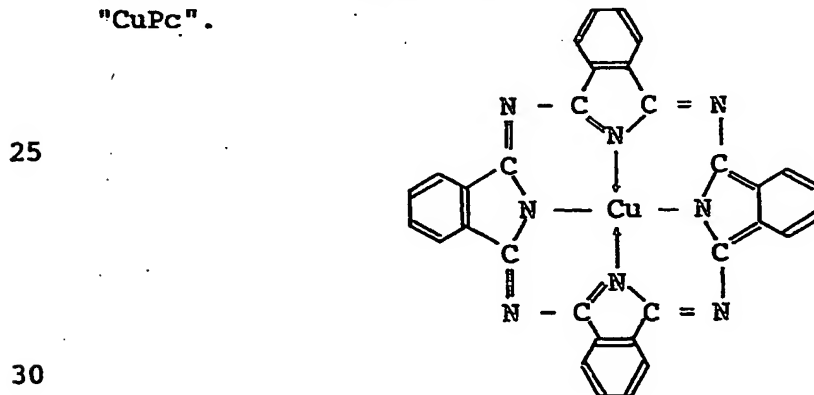
As the highly water-absorbing material employed in this invention, a highly water-absorbing polymers are preferred, which may be, for example, graft-copolymers of starch/sodium acrylate, copolymer salts of isobutylene/maleic anhydride, copolymer salts of styrene/maleic anhydride, cross-linked sodium polyacrylate, graft-copolymers of polyvinyl alcohol/acrylate, saponified copolymers of vinyl ester/ethylenically unsaturated carboxylic acid or its derivative, and the like. Particularly, high molecular weight electrolytes containing carboxylate salt are polymers with a high rate of water-absorbing capacity, and yet have an excellent strength even after having absorbed water. They are preferred materials for this purpose. An example is "Sumikagel F-33", produced by Sumitomo Chemical Co., Ltd. or cross-linked sodium polyacrylate.

In this invention, it is optional to co-use a material publicly known in the filter technology, such as activated carbon.

5 The filter according to this invention effectively removes by adsorption harmful or hazardous substances present in tobacco smoke, for example, harmful aromatic compounds and heterocyclic compounds, in particular, those
10 compounds having two, particularly more than two, aromatic rings, such as benzopyrene, preferably in the presence of moisture, though the absence of moisture is not a precluding condition.

In this invention, the tobacco filter may usually
15 be present in a cigarette holder or pipe, but, depending on the type of the material used, it may be equipped at one end of cigarette.

Phthalocyanine used in this invention, for
20 example, copper phthalocyanine, may be shown as a compound having the following skeleton, hereinafter referred to "CuPc".

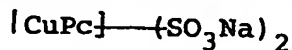


Phthalocyanine compounds used in this invention are described as pigments or dyes in literatures, for example, on pages 316 - 1109 of the New Edition, "Dyestuff
35 Guidebook" edited by the Synthetic Organic Chemistry Association, Maruzen Co., Ltd., published on July 20, 1970,

or the Color Index. As concrete examples, the following compounds may be cited.

A. Dyes:

- 5 C.I. Direct Blue 86 (direct dye)

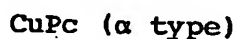


- C.I. Vat Blue 29 (vat dye)

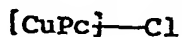
(Nihonthrene Brilliant Blue 4G paste: made by
10 Sumitomo Chemical Co., Ltd.)

B. Pigments:

- C.I. Pigment Blue 15



- 15 $\text{CuPc } (\beta \text{ type})$

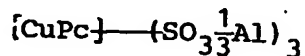
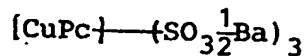


- C.I. Pigment Blue 16

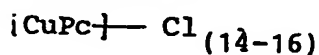


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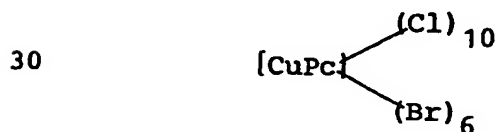
- C.I. Pigment Blue 17



- 25 C.I. Pigment Green 7



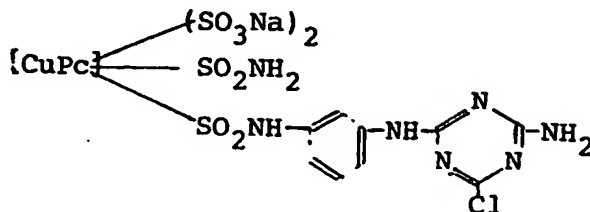
- C.I. Pigment Green 36



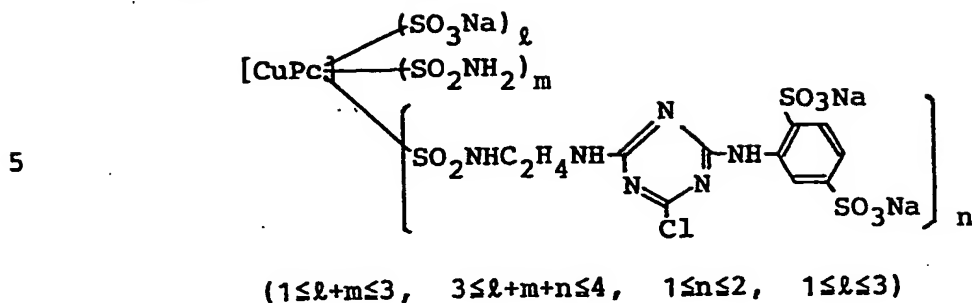
C. Reactive dyes:

- C.I. Reactive Blue 7

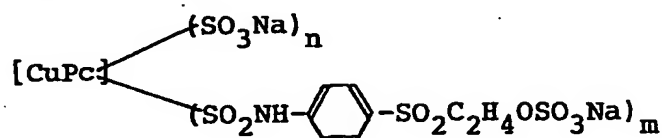
35



C.I. Reactive Blue 15



10 C.I. Reactive Blue 21



15

$$(1 \leq n \leq 3, 1 \leq m \leq 2, 2 \leq m + n \leq 4)$$

C.I. Reactive Blue 75

(Cibacron Pront Turquoise G: a reactive dye made by Ciba Geigy A.G.)

20

C.I. Reactive Blue 116

(Levafix Turquoise Blue E-BA: a reactive dye made by Bayer A.G.)

25 C.I. Reactive Blue 118

(Sumifix Turquoise Blue GS: a reactive dye made by Sumitomo Chemical Co., Ltd.)

C.I. Reactive Blue 148

30 (Sumifix Turquoise Blue BF: a reactive dye made by Sumitomo Chemical Co., Ltd.)

C.I. Reactive Blue 105

35 (Levafix Turquoise Blue P-BRA: a reactive dye made by Bayer A.G.)

C.I. Reactive Blue 18

(Cibacron Turquoise Blue TG-E: a reactive dye
made by Ciba Geigy A.G.)

5 C.I. Reactive Blue 41

(Cibacron Turquoise Blue 2G-E: a reactive dye
made by Ciba Geigy A.G.)

C.I. Reactive Blue 71

10 (Procion Turquoise Blue H-A: a reactive dye
made by I.C.I. Co.)

C.I. Reactive Blue 25

15 (Procion Brilliant Blue H-5G: a reactive dye
made by I.C.I. Co.)

C.I. Reactive Blue 80

20 (Levafix Turquoise Blue E-4G: a reactive dye
made by Bayer A.G.)

C.I. Reactive Blue 3

(Procion Brilliant Blue H-7G: a reactive dye
made by I.C.I. Co.)

25 C.I. Reactive Blue 72

(Cibacron Turquoise Blue GR-D: a reactive dye
made by Ciba Geigy A.G.)

30 These dyes may be added, adhered, or bound to
the substrate by the known methods. For example, a
reactive dye may be bound to a cellulose substrate in
a water medium in the presence of an alkali agent.

35 In this invention, when a pigment sold on the
market is used for the phthalocyanine compound, such
product usually contains various impurities which have

contaminated into them during their production steps, or it has been given a surface treatment suitable for their usages. Therefore, it is desirable to extract or wash the product by a solvent before use. When a filter
5 material is dyed with the dyes, it is desirable to rinse the dyed member with an aqueous medium, so that the dye should not disengage easily when the member is used for the purpose of this invention.

10 The phthalocyanine compound thus obtained may be placed in the filter material, preferably in wet atmosphere, though dry atmosphere is not precluded.

15 Further detailed description on the embodiment of this invention will be given below in respect with the working examples and references.

Reference (1)

20 Into 600 ml of water placed in a 1 liter beaker was added 30 g of sanitalized cotton. The mixture was slowly agitated and heated up to 30°C. Then, 2 g of "Sumifix Turquoise Blue G" (a reactive dye made by Sumitomo Chemical Co., Ltd.: Color Index (C.I.), Reactive Blue 21), and 30 g of anhydrous sodium sulfate were added thereto.
25 The mixture was agitated for 20 minutes. Then, 12 g of sodium carbonate was added thereto. After agitation for 15 minutes at 30°C, the temperature of the mixture was raised to 70°C during 20 minutes. The reaction was allowed to continue for 60 minutes at 70°C, before the
30 completion of the reaction. The blue colored cotton was separated by filtration using a Buchner funnel, and put into 900 ml of water containing 1.8 g of "Monogen" (a detergent made by Daiichi Kogyo Seiyaku Co., Ltd.: sodium alkylbenzenesulfonate). The soaping was effected for 5
35 minutes at 100°C. The cotton was separated by filtration using a Buchner funnel, rinsed extensively with water, and

dried. The cotton was then washed sequentially with dimethylsulfoxide, methanol-concentrated hydrochloric acid (volume ratio 50:1), methanol-concentrated ammonia water (volume ratio 50:1) and methanol, until the washing
5 liquids gave no coloration. Then, the cotton was dried.

The blue sanitalized cotton thus obtained was subjected to the analysis of its copper content according to the atomic absorption spectrum method. The content
10 of copper was 0.065 %. Accordingly, 1 g of the cotton should contain 1.0×10^{-6} mol of phthalocyanine unit. This material is hereafter referred to as "blue-cotton A".

Reference (2)

15 One liter of water, 25 g of anhydrous Glauber's salt and 1 g of C.I. Direct Blue 86 ("Sumilight Supra Turquoise Blue G conc": a product of Sumitomo Chemical Co., Ltd.) were placed in a 2 liter beaker, and they were made dissolved by agitation. Then, 50 g of sanitalized
20 cotton was immersed into the thus prepared dye bath, and the temperature was held at 95°C for 60 min. under agitation. Then the cotton was rinsed with water and dried to obtain a blue colored cotton (hereafter called "blue cotton B").

25

Reference (3)

One hundred parts of C.I. Vat Blue 29 ("Nihon-threne Brilliant Blue 4G Paste": made by Sumitomo Chemical Co., Ltd.) and one part of sodium alginate were added to water
30 to prepare 100 parts of a dye bath. A cotton broadcloth was immersed into this dye bath and was squeezed to 60 % squeeze rate and then dried in hot air at 105°C.

Separately, 60 parts of "Hydrosulfite Conc"
35 (made by Sumitomo Chemical Co. Ltd.), 30 parts of caustic soda and 60 parts of sodium chloride were dissolved in

water to prepare 1000 parts of a bath. The cotton broad-cloth to which the dye had been adhered, was immersed into the bath and then squeezed to 120 % squeeze rate. It was then given a steam treatment for 30 seconds in 105°C saturated steam to cause a reduction dyeing. After water-rinsing, the thus-treated adsorbent cloth was subjected to an oxidation treatment at 50°C in 1000 parts of a bath prepared by dissolving 10 parts of hydrogen peroxide (35 %) and 10 parts of acetic acid (48 %) into water. Then, it was subjected to soaping for 5 min. at 95°C in 1000 parts of water containing 3 parts of "Monogen". (a product of Daiichi Kogyo Seiyaku Co.). The cloth was thoroughly rinsed again with water and dried to obtain a blue colored cotton broadcloth (hereafter called "blue broadcloth").

Reference (4)

One liter of water, 25 g of anhydrous Glauber's salt and 1 g of C.I. Direct Blue 86 ("Sumilight Supra Turquoise Blue G Conc": a product of Sumitomo Chemical Co.) were put into a 2 liter beaker, and the mixture was agitated for dissolution. Then, 50 g of a nylon fiber was immersed into such dye bath, and 0.5 g of acetic acid was added thereto. The temperature was held at 95°C for 60 min. under agitation. Then, water was squeezed out to obtain a wet blue colored nylon fiber (hereafter called "blue nylon").

Reference (5)

Into a kneader were charged 200 g of copper phthalocyanine, 1,200 g of sodium chloride and 350 g of diethylene glycol, and the mixture was ground for 6 hours. The ground content in the kneader was charged into 5 liters of water, and the undissolved portion was separated by filtration, rinsed with water, and washed with various solvents. The thus-pulverized copper

were measured by the following methods. Using a constant flow rate smoking device, a smoking was effected under such conditions that the smoking period of time is 2 sec. per each suction, with intervals between the suctions are each 40 sec., smoking length is 50 mm, and smoke flow rate is 16 ml/sec. The main streams of the smoke of 4 tubes were collected with one Cambridge Filter CM 113, and the amount of tar was measured by a weight method.

10

$$\text{Rate of removal of tar} = \frac{(\text{amount caught by tobacco filter}) \times 100}{(\text{amount caught by Cambridge filter}) + (\text{amount caught by tobacco}) + (\text{amount caught by tobacco filter})}$$

15

The measured value is the mean value of 20 cigarettes, and the third digit of effective number was rounded by the rule of counting fractions of 0.5 and over as a unit and cutting away the rest. The rate of removal of mutagens was measured by mutagenicity revealed by the Ames Test. The strain used in the test was TA 98, and the number of revertant colonies was measured with a condition of the tar caught in the Cambridge filter of 300 µg/plate S9 : 80 µl/plate.

25

$$\text{Rate of removal of mutagens} = \left[1 - \frac{(\text{Number of colonies in tar collected in Cambridge filter when filter was used})}{(\text{Number of colonies in tar collected in Cambridge filter when no filter was used})} \right] \times 100$$

30

The suction resistance was measured against the stream at the flow rate of 20 ml/sec. using a aeration resistance meter.

35 Example 2

A tobacco filter was prepared with each of the

materials obtained in the References and a highly water-absorbing material. It was packed in a glass tube with inner diameter of 8 mm and a length of 15 mm. The thus-prepared glass tube with the filter was fixed on a
5 constant flow rate smoking device. The results obtained are shown in Table 2.

The results indicate that all cases have the effectiveness for the removal of mutagens selectively,
10 when compared with the case where no copper phthalocyanine compound was present.

Table 2

15	Composition of filter	Rate of removal of tar %	Rate of removal of mutagens %	Suction resistance mm H ₂ O
	Fiber mixture with "Blue Cotton A" and "Sumikagel"*	35	41	47
20	Fiber mixture with "Blue Cotton B" and "Sumikagel"*	33	36	45
25	Fiber mixture with pigment and "Sumikagel"*	36	39	51

(Note): Sumikagel : Containing 5 wt.% of "Sumikagel F-33"
(a highly water-absorbing polymer made
by Sumitomo Chemical Co., Ltd.)

30 In the above table, the methods employed to measure the rate of removal of tar, the rate of removal of mutagens and the suction resistance were the same as those employed in Example 1.

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CLAIMS

1. A tobacco filter, characterized by the presence of a phthalocyanine compound in the material of the filter.
2. A tobacco filter according to claim 1, wherein the phthalocyanine compound is a reactive dye.
3. A tobacco filter according to claim 1 or 2, wherein the phthalocyanine compound is a water-soluble copper phthalocyanine compound.
4. A tobacco filter according to claim 1, 2 or 3 wherein the phthalocyanine compound adheres to or is chemically bound to the filter material.
5. A tobacco filter according to any one of the preceding claims wherein the filter material is a substance containing hydroxyl or amino groups.
6. A tobacco filter according to claim 1, wherein the filter material is a polyhydroxy compound or derivative thereof.
7. A tobacco filter according to any one of the preceding claims, which comprises a water-absorbing polymer compound as a highly water-absorbing material.
8. A tobacco filter according to claim 7, wherein the water-absorbing polymer compound is a polymer electrolyte containing carboxylate salt groups.
9. A tobacco filter according to claim 8, wherein the highly water-absorbing material is a cross-linked sodium polyacrylate.
10. A tobacco filter according to any one of the preceding claims, wherein water is present in the filter material.
11. An article for smoking, in the form of a cigarette, cigarette holder or pipe, comprising a tobacco filter as claimed in any one of the preceding claims.